



Office of Research and Development
National Risk Management Research Laboratory
Air and Energy Management Division

**Joint ORD/New York State Department of Environmental
Conservation: Saint-Gobain PTFE Sintering Facility
Emissions Characterization Study**

Method Development/Measurements
QA Category A

Intramural Research

Revision Number: 0

Date:

November 27, 2018

Prepared by:

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ORD National Program A-E

QA Track ID

G-AEMD-0031868-QP-1-0

NRMRL

Quality Assurance Project Plan (QAPP)

Title:	Joint ORD/New York State Department of Environmental Conservation: Saint-Gobain PTFE Sintering Facility Emissions Characterization Study		
Division/Staff:	AEMD\SSB		
QA Category:	A		
ORD National Program:	A-E		
RAP Project ID\Task ID:	Assigned at the project & task level		
QAPP Tracking Number:	G-AEMD-0031868-QP-1-0		
Effective Date:	November 27, 2018		
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Notice

This document is intended for internal Agency use only. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

List of Abbreviations

ADQ	Audit of Data Quality
A-E	Air and Energy National Program
AEMD	Air and Energy Management Division
AQB	Air Quality Branch
CIM	Chemical Ionization Mass Spectrometry
CoC	Chain of Custody
DAR	Department of Air Resources
DSBB	Distributed Source and Buildings Branch
EMMD	Exposure Methods & Measurements Division
EPA	U.S. Environmental Protection Agency
FTOH	Fluorotelomer alcohols
GC/MS	Gas Chromatography/Mass Spectrometry
HASP	Health and Safety Plan
HF	Hydrofluoric acid
HFP	Hexafluoropropylene
IEIB	Internal Exposure Indicators Branch
IS	Internal standard
LRB	Laboratory Research Note Book
NERL	National Exposure Research Laboratory
NIST	National Institute of Standards and Technology
NRMRL	National Risk Management Research Laboratory
NYSDEC	New York State Department of Environmental Conservation
ORD	Office of Research and Development
PFA	Perfluoroalkoxy
PFAA	Perfluorinated alkyl acids
PFAS	Per-/Poly-Fluoro alkylated Substances
PFC	Perfluorinated Compound
PFCAs	Polyfluorinated carboxylic acids
PFOA	Perfluorinated Octanoic Acid
PFOS	Perfluorooctane Sulfonate
PFTBA	Perfluorotributylamine
PHCB	Public Health Chemistry Branch
PI	Principal Investigator
PPM	Policies and Procedures Manual
pQAPP	Programmatic Quality Assurance Project Plan
PTFE	Polytetrafluoroethylene
QA	Quality Assurance
QAM	Quality Assurance Manager
QAPP	Quality Assurance Project Plan
QC	Quality Control
RT	Retention time
SHEM	Safety, Health and Environmental Management
SIM	Selective ion monitoring
S/N	Signal to noise ratio
SOP	Standard Operating Procedure
SSB	Stationary Source Branch
TFE	Tetrafluoroethylene
TSA	Technical Systems Audit
VOC	Volatile Organic Carbon

**Quality Assurance Project Plan for Joint ORD/New York State Department of Environmental
Conservation: Saint-Gobain PTFE Sintering Facility Emissions Characterization Study**

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Preface

This QAPP is associated with the Quality Assurance Program Plan (pQAPP): Programmatic Quality Assurance Project Plan for Per- and Polyfluorinated Alkyl Substances Research in NRMRL (QAPP ID: G-IO-0031626-QP-1-5) and serves as the plan for sampling and analysis of air emissions, by NRMRL, NERL and NYSDEC scientists, from the Saint-Gobain PTFE Sintering Facility in New York.

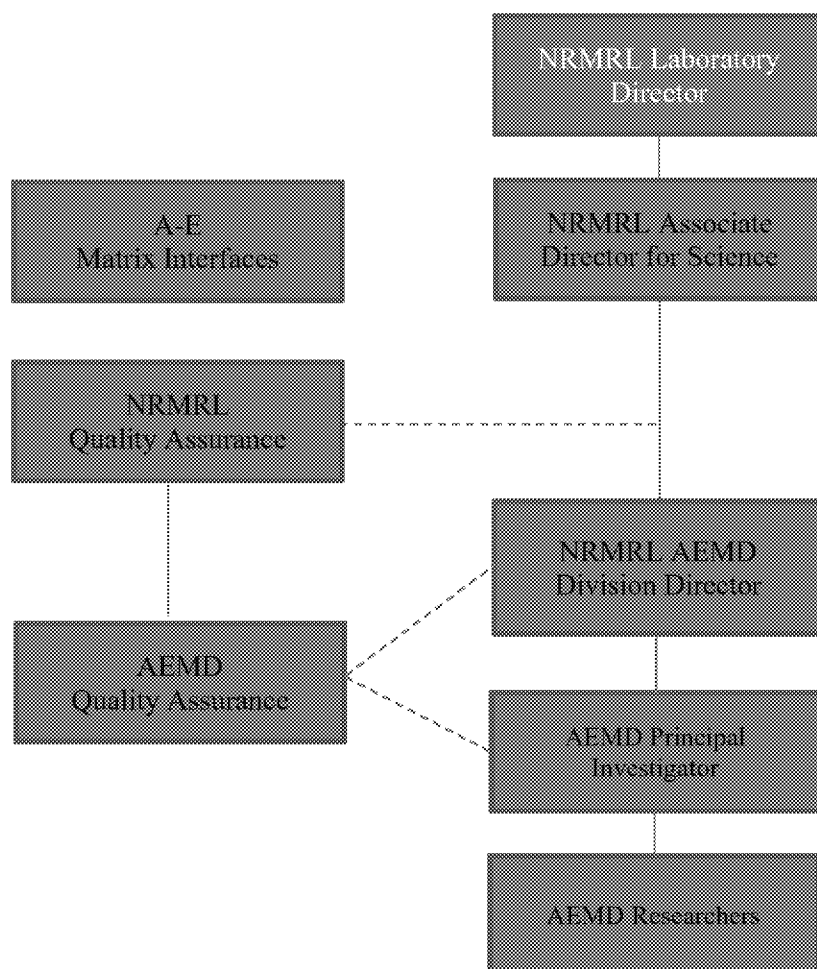
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A4. Project/Task Organization

Organization structure will adhere to the NRMRL pQAPP, reporting lines for AEMD are shown in Figure 1.

Figure 1: NRMRL AEMD PFAS Research Program Organizational Chart



Roles and responsibilities of EPA personnel for the Saint-Gobain project are summarized below:

Project Personnel	Role	Responsibility
Jeff Ryan	AEMD Principal Investigator	Overall project development; Coordinate project discussions between AEMD, EMMD, R2 and NYSDEC, on-site sampling, data reporting
John Offenberger	EMMD Principal Investigator	Project development and guidance, data reporting
Mark Strynar	EMMD Principal Investigator	Targeted and non-targeted PFAS analysis & data reporting
Ingrid George	AEMD Principal Investigator	VOC analysis & data reporting/review
Theran Riedel	EMMD Principal Investigator	PFCA and FTOH analysis & data reporting/review
Andrew Lindstrom	EMMD Principal Investigator	Project guidance
Ken Krebs	AEMD Chemist	On-site sampling, sample analysis, data reporting/review
Dennis Tabor	AEMD Chemist	Data review
Jackie Rosati Rowe	EPA project supervision	EPA Project oversight and approval
Richard Shores	EPA project supervision	EPA Project oversight and approval
Libby Nessley	AEMD QA Manager	Advises on QA requirements, reviews and approves project QAPP and associated SOPs
Sania W. Tong Argao	EMMD QA Manager	Advises on QA requirements and associated SOPs
Timothy Buckley	EMMD Coordinator	Coordinate EMMD activities
Brian Gullett	AEMD Coordinator	Coordinate AEMD activities
Tom Gentile	NYSDEC Coordinator	Project development and guidance; coordination with Test Facility
Ben Potter	NYSDEC Coordinator	Project development and guidance; coordination with Test Facility
John DiMartino	Regional supervision (R2)	Assist with overall project coordination and to help lead efforts to communicate project results to NYSDEC and R2 constituents

A5. Problem Definition/Background

PFAS include a wide variety of manufactured compounds commonly used to make products more resistant to stains, grease and water. PFAS are also a key constituent in aqueous film forming foams used in fire suppressants. PFAS have been used to make non-stick cookware, waterproof clothes and mattresses, stain resistant carpets and fabrics, firefighting materials, and are used as a friction reducer in the aerospace, automotive, construction and electronics industries. The most commonly studied PFAS are perfluorinated octanoic acid (PFOA) and perfluoro octane sulfonate (PFOS). In addition to PFOA and PFOS, other perfluorinated alkyl acids (PFAAs), fluorotelomer alcohols, per- and polyfluorinated ethers, and perfluoro octane sulfonamides may be present in products as manufacturing residuals and transformation products. PFOA and PFOS are extremely persistent in the environment and in the human body. Half-lives for PFOA and PFOS in the human body can be as long as several years. PFAS are also believed to be resistant to many common wastewater treatment processes.

Health studies have indicated that PFAS are toxic to mammals, including humans. Coupling this fact with their ubiquitous and highly persistent nature makes PFAS an important emerging class of contaminants of concern for the EPA and other environmental regulatory organizations.

A6. Project/Task Description

New York State Department of Environmental Conservation (NYSDEC), Department of Air Resources (DAR) and EPA Region 2 have requested EPA Office of Research and Development (ORD) support to qualitatively characterize potential residual PFAS and thermal decomposition product emissions from a polytetrafluoroethylene (PTFE) sintering process. Specifically, ORD has been requested to perform targeted and non-targeted PFAS analyses, including PFOA, as well as targeted and non-targeted volatile organic compounds (VOCs) to identify compounds present in process emissions. Quantitative analyses are not within the scope of this study.

The process studied is an industrial source where bulk PTFE (~1,000 lb) is molded and then sintered in an oven. The sintering process involves a gradual heating of the PTFE billet until reaching the desired sintering temperature (~700 °F). The overall sintering process requires ~5 days. During the sintering process, emission products generated are vented directly to the atmosphere. Potential emissions include residual PFAS as well as thermal degradation products such as hydrofluoric acid (HF), and PTFE monomers. Emissions samples will be collected by ORD and NYSDEC personnel and analyzed by ORD personnel to qualitatively screen for emissions of interest.

A7. Quality Objectives

The objectives of this joint ORD – NYSDEC study are to characterize the emissions, as comprehensively as possible, from the PTFE sintering process. This includes characterizing emissions as a function of sintering oven temperature. Investigating the potential presence of PFOA is the primary targeted measurement as well as the presence of thermal degradation products such as tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and perfluoroisobutylene (PFIB).

A secondary objective of this study is to investigate on-line, real-time chemical ionization mass spectrometry (CIMS) as a potential process monitor for temporal process emission characterization.

The results of the program will be used to qualitatively identify the specific PFAS compounds and related byproducts, including the products of PTFE thermal decomposition associated with air emissions from the sintering process. NYSDEC will utilize this information to:

- (1) Document emissions of fluorinated compounds utilizing current chemical formulations of PTFE powders; and
- (2) Determine whether conditions warrant the installation of air pollution controls to minimize any potential environmental and public health impacts.

A8. Special Training/Certification

No specific training is required for this project, but the analysts shall have completed all site-specific health and safety training requirements that are applicable and be competent in the operations of the analytical instrumentation being used. Records of this training are maintained by the EPA SHEM office or by individual researchers, respectively. This document assumes laboratory personnel will have a thorough working knowledge of basic laboratory skills, reagents, and instrumentation. Any standard operating procedures (SOPs) utilized are designed to guide a competent laboratory worker in the analysis of per- and polyfluorinated compounds and it is not intended to instruct individuals on the basic aspects of analytical chemistry.

A9. Documents and Records

AEMD will follow the procedures as detailed in the overall NRMRL pQAPP. Specifically, for this study, the

following approaches will be employed.

Planning Documents

This QAPP is the planning document for this study. Additional documentation will be maintained in laboratory research notebooks (LRBs), chain of custody (CoC) forms, and the study file. Any necessary modifications to QAPP procedures and approaches while in the field or other phases of study implementation will be described in the appropriate LRBs.

Tracking Documents

All study information will be recorded and tracked in a dedicated study file. This information will be maintained by the AEMD PI, Jeff Ryan, and will include copies of the sampling data logs, the field sample tracking forms, and the laboratory records describing the preparation and deployment of field quality control (QC) samples. All analysts will maintain sample preparation records and analysis logs. The CoC forms will be used to track the samples transported to the EPA/RTP analytical laboratories and these forms will be retained by EPA after analysis. The study file will also contain the records of QA issues, amendments to plans and SOPs, audit reports, and corrective action reports. QA records, such as audit reports, corrective action reports, etc., will be maintained by the EPA PIs. Finally, John Offenberger (NERL/EMMD) and Mark Strynar (NERL/EMMD) will maintain the study file documentation together with all associated final reports. All records will be maintained according to EPA specifications.

The LRBs are where records of field sampling and laboratory analytical activities, including sample run collection notes, the extraction and preparation of samples for analysis, the preparation of sampling containers (when appropriate), and the preparation of standard solutions for spiking, and calibration are documented. Methods and reagents used are recorded and appropriate SOPs used for analysis are also cited.

The Sample Analyses records are the instrument logs that document the analyses of samples, and contain records of specific instrument conditions, and date and time of sample data acquisition. Additional information or details on sample analyses may be documented in LRBs.

Section B. Data Generation and Acquisition

B1 Sampling Process Design (Experimental Design)

Multiple gaseous emissions samples will be collected at the sintering process uncontrolled exhaust. Emissions samples will be collected as a function of sintering process temperature and time at each temperature. The time integrated whole air and aqueous impinger emissions samples cannot be collected continuously, but can be collected for ~30-120 min intervals for each Test Condition window. With the exception of Test Condition 1 (~30 min), single, time integrated whole air and aqueous impinger samples will target ~120 min run times for Test Conditions 2-8. Multiple, time integrated whole air and aqueous impinger samples targeting ~120 min will be collected for Test Conditions 9-11. The actual number of samples will be limited to ~16 discrete time integrated whole air and aqueous impinger samples. On-Line CIMS process emissions measurement and monitoring will be attempted for the entire duration of the ~67.5h sintering process. An example of the planned sampling schedule is presented in Table 1. The final and actual schedule will be established during the field test and is largely dictated by the process temperature profile as well as on-site field personnel availability.

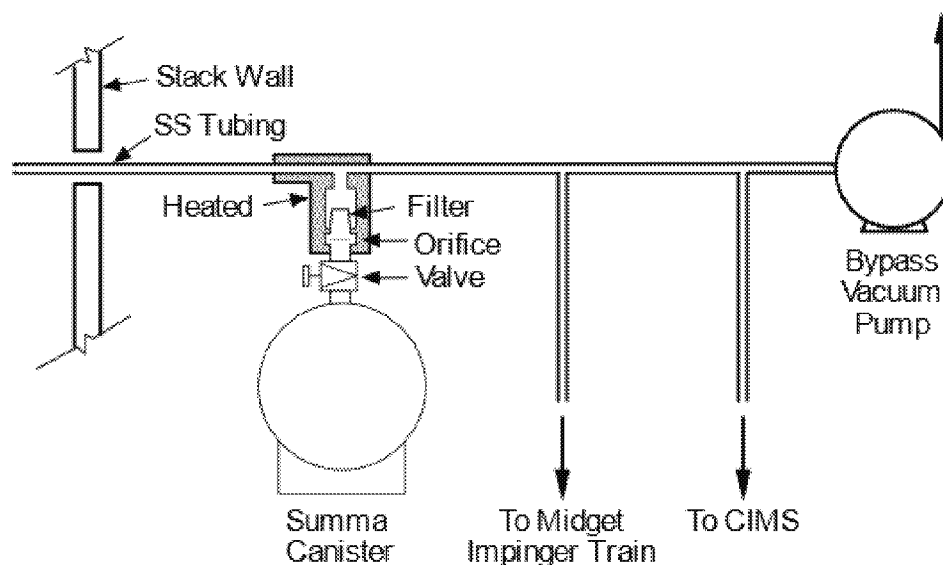
Table 1. Sampling Schedule

Test Condition	Temperature (F°)	Δ Time (h)	Cumulative Time (h)	Sample Number	Target Sample Time (h)
Baseline	200	0	0.0	-	-
1	200 - 250	0.5	0.5	1	0.5
2	250 - 300	2.25	2.75	2	2
3	300 - 350	1.75	4.5	3	1.5
4	350 - 400	2.5	7	4	2
5	400 - 450	2.5	9.5	5	2
6	450 - 500	2.0	11.5	6	2
7	500 - 550	2.0	13.5	7	2
8	550 - 600	3.5	17	8	2
9	600 - 650	8.75	25.75	9, 10	4
10	650 - 700	5.5	31.25	11, 12	4
11	Hold 700	36.25	67.5	13 - 16	8
Cool down	N/A	52.5	120		30 h total

Oven temperature data and time intervals will be determined and recorded by St. Gobain personnel and provided to NYSDEC. PTFE billet weight will be recorded before and after sintering process by St. Gobain personnel and provided to NYSDEC.

B2 Sampling Methods

All samples will be collected from a sampling manifold where the process emissions are extracted from the stack with a dedicated sampling system. The sampling system, depicted in Figure 2, consists of an unheated sample probe (¼" OD SS) and heated ¼" OD SS tubing from the probe to the heated (~250 F) manifold (also comprised of ¼" OD SS tubing). The emissions sample is withdrawn from the stack with a bypass vacuum pump and a sample flow of 6 – 8 Lpm. All emissions samples are collected from the vacuum side of the sample pump. The total emissions sample flow is well less than the bypass flow. It should be noted that the exact distance from the probe to the sampling manifold is unknown at this time and is assumed to be within a few feet from the stack. If not, a longer length of ¼" OD heated PFA Teflon tubing may be needed and cannot be avoided. Regardless, the system background contamination will be measured by introducing nitrogen through the entire sampling system and collecting the associated samples.

Figure 2. Sampling System

SUMMA Canister Sampling

Whole air samples with SUMMA canisters will be collected for TO-15 targeted qualitative analyses (GC/MS), targeted qualitative TFE, HFP and PFIB analyses (GC/MS) and qualitative PFAS screening using CIMS. Samples will be collected at nominally 40 cc/min with a total sample volume of ~4–5L. As a result, sampling durations of up to ~120 min are possible. Samples will be collected from a manifold connected to a bypass sampling system. Specific details on the sampling system and sampling approach are contained in INTERNAL NRMRL/AEMD PROCEDURE: *Collection of Whole Air Emissions Samples for VOC and PFAS Analysis Using SUMMA Canisters* (See attached). System blanks, injecting nitrogen at the probe and through the entire sampling system will be used to characterize background contamination. Each and every SUMMA canister used for this study will be cleaned and blanked for all intended analytical approaches. Details on the SUMMA canister cleaning process are found in ECAB-133: Standard Operating Procedure for Cleaning Air Sampling Canisters with the Entech 3100A Canister Cleaner.

Midget Impinger Sampling

An aqueous, four-impinger, midget impinger train will be used to collect hydrophilic PFAS for targeted and non-targeted, qualitative PFAS analyses. The first three impingers will contain deionized water, with the fourth impinger containing silica gel (dessicant). This approach focuses on the collection of hydrophilic PFAS compounds, including PFOA, that may be present in the PTFE sintering process exhaust and is not intended to quantitatively capture all potential PFAS compounds. Specific details on the sampling system and sampling approach are contained in INTERNAL NRMRL/AEMD PROCEDURE: *Collection of Hydrophilic PFAS Emission Samples for PFAS Analysis Using Midget Impingers* (In preparation).

On-Line Chemical Ionization Mass Spectrometry Process Emissions Measurement and Monitoring

ORD/NERL's iodide adduct high resolution CIMS will be used as a real-time, on-line process characterization monitor. It is the same system that will be used to analyze the SUMMA canisters. The CIMS is capable of detecting polar compounds such as polyfluorinated carboxylic acids (PFCAs), including PFOA, as well as fluorotelomer alcohols (FTOHs). Specific details on the measurement approach are contained in the NERL/QAPP Measurements of polar per- and polyfluoroalkyl substances (PFAS) in the gas

and liquid phase by iodide-adduct chemical ionization mass spectrometry (CIMS) QA Tracking # D-EMMD-0031657-QP-1-0 as well as “Operation of the Aerodyne/Tofwerk Chemical Ionization Mass Spectrometer” (#D-EMMD-AQB-013-SOP-02). For these specific tests, the CIMS will withdraw its sample from the same sampling manifold used for the SUMMA canister sampling as well as the midget impinger sampling. A heated sampling line may be needed to transfer the emissions gas sample to the CIMS if the CIMS cannot be located in the vicinity of the sampling manifold. The heated sampling line will be made from perfluoroalkoxy (PFA) fluoropolymer rather than PTFE fluoropolymer to avoid/minimize potential background contamination. System blanks, injecting nitrogen at the probe and through the entire sampling, including heated sample line if needed, will be used to characterize background contamination.

B3 Sample Handling and Custody

Sample Custody

EPA/ORD personnel are responsible for all sample handling and custody activities. ORD field researchers will label all samples with unique identifiers and will prepare all Chain of Custody (CoC) forms and keep a copy for record. The sample IDs are defined by the field collectors. Laboratory staff will use these assigned sample IDs and will not assign new sample identification numbers. CoC forms will be shipped with samples and include information such as collected by name/date, shipped by name/date, and received by name/date plus any additional sampling information necessary to document sampling time, date, duration, location and special comments (e.g., sample leak). Upon receipt at the laboratory, the sample custodian will check the contents of each shipping container for sample container breakage and will verify that contents match the shipping lists. After logging in each sample, and signing CoC forms, the samples will be transferred to the appropriate storage facility.

Sample Storage

SUMMA canisters will be stored at temperatures above freezing at all times and will be stored at laboratory room temperature prior to analysis. The aqueous impinger samples will be transported in ice chilled coolers and will be stored in a refrigerator at less than 4 °C prior to analysis. No holding times are applicable to the samples.

B4 Analytical Methods

Targeted TO-15 VOCs by GC/MS

Targeted GC-MS analysis of the SUMMA canisters for TO-15 VOCs will be conducted on a GC coupled to a quadrupole and/or time-of-flight mass spectrometer. The targeted VOC compounds are presented in Table 2. Both GC-MSs will be tuned and calibrated using perfluorotributylamine (PFTBA), according to the manufacturer’s instructions, before each sample set. Samples will be analyzed under selective ion monitoring (SIM), electron ionization-MS conditions. Details of Method TO-15 is contained in *EPA/625/R-96/010b: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-15 Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)*. Details of the equipment-specific analyses are found in *ECAB-144: Standard Operating Procedure for Determination of Volatile Organic Compounds in Whole Air Samples Collected in Canisters Using the Agilent 6890/5973N GC-MSD*. Chromatographic retention times and ‘area under the curve’ will be reported for each tentatively identified compound. No internal standard masses (i.e. ‘mass added’), nor peak areas will be reported even if added to these samples.

Table 2. TO-15 Target VOCs

Propylene	Methylene Chloride	2-Methylhexane	Bromoform
Propane	3-Chloro-1-Propene	2,3-Dimethylpentane	Styrene
Dichlorodifluoromethane	1,1,2-Trichloro-1,2,2-...	Tert Amyl Methyl Ether	1,1,2,2-Tetrachloroethane
Chloromethane	Carbon Disulfide	3-methylhexane	o-Xylene
Isobutane	2,2-Dimethylbutane	1,2-Dichloropropane	Nonane
Dichlorotetrafluoroethane	trans-1,2-Dichloroethene	Bromodichloromethane	Bromofluorobenzene
Vinyl Chloride	Cyclopentane	1,4-Dioxane	Chlorotoluenes
1-Butene	2,3-Dimethylbutane	Trichloroethene	n-Propylbenzene
1,3-Butadiene	1,1-Dichloroethane	Isooctane	m-Ethyltoluene
Butane	Methyl-t-Butyl-Ether	Methyl Methacrylate	1,3,5-Trimethylbenzene
trans-2-butene	Vinyl Acetate	Heptane	1,2,4-Trimethylbenzene
Bromomethane	2-Methylpentane	cis-1,3-Dichloropropene	Tert-Butyl Benzene
cis-2-butene	2-Butanone	4-Methy-2-Pentanone	1-Ethyl-4-Methyl Benzene
Chloroethane	3-Methylpentane	Methylcyclohexane	o-Ethyltoluene
Ethanol	2-Chloroprene	trans-1,3-Dichloropropene	1,3-Dichlorobenzene
Vinyl Bromide	1-Hexene	1,1,2-Trichloroethane	1,4-Dichlorobenzene
Acetonitrile	cis-1,2-Dichloroethene	2,3,4-Trimethylpentane	n-Decane
Acrolein	Diisopropyl ether	Toluene	Sec-Butyl Benzene
Acetone	Ethyl Acetate	2-Methylheptane	1,2,3-Trimethylbenzene
iso-Pentane	n-Hexane	2-Hexanone	1,2-Dichlorobenzene
Trichlorofluoromethane	Chloroform	Dibromochloromethane	o-Cymene
Isopropyl Alcohol	Tetrahydrofuran	3-Methylheptane	1,3-Diethylbenzene
1-Pentene	Ethyl Tert-Butyl Ether	1,2-Dibromoethane	1,2-Diethylbenzene
Acrylonitrile	Methylcyclopentane	Octane	n-Butyl Benzene
n-Pentane	1,2-Dichloroethane	Tetrachloroethene	Undecane
Isoprene	2,4-Dimethylpentane	1,1,1,2-Tetrachloroethane	1,2,4-Trichlorobenzene
trans-2-pentene	1,1,1-Trichloroethane	Chlorobenzene	Naphthalene
cis-2-pentene	Benzene	Ethylbenzene	Dodecane
Tert-Butanol	Carbon Tetrachloride	m-Xylene	Hexachlorobutadiene
1,1-Dichloroethene	Cyclohexane	p-Xylene	

Targeted and non-Targeted Thermal Degradation Products by GC/MS

Targeted GC-MS analysis of the SUMMA canisters for TFE, HFP, and PFIB will be conducted on a GC coupled to a quadrupole and/or time-of-flight mass spectrometer. Both GC-MSs will be tuned and calibrated using perfluorotributylamine (PFTBA), according to the manufacturer's instructions, before each sample set.

Samples will be analyzed under full-scan (e.g. m/z 50-950 or the instrument specific full scan range as applicable), electron ionization-MS conditions. Gas standards for TFE and HFP will be used to aid in compound identification/compound absence. As no gas standard for PFIB will be used, tentative identification/compound absence will be determined with the aid of reference spectra and retention indices. The compound E1 (Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether) may also be included as a target compound. E1 is the known thermal degradation product of the HFPO-DA ammonium salt which may be a residual compound from PTFE production. Instrument parameters that are analyte-specific will be recorded in the instrument log book and LRB of PI (or approved user). Method development and methods deemed appropriate for non-targeted analysis will be recorded in the LRB of the PI. Preliminary identification of compounds will be completed by recording the m/z values of peaks of interest, compared to in house, putative identification databases. Chromatographic retention times and 'area under the curve' will be reported for each tentatively identified compound. No internal standard masses (i.e. 'mass added'), nor peak areas will be reported even if added to these samples.

PFCAs and FTOHs

CIMS analysis for PFCAs, including PFOA, and FTOHs will be conducted on an Aerodyne CIMS high resolution mass spectrometer. Specific details on the measurement approach are contained in the NERL/QAPP "Measurements of polar per- and polyfluoroalkyl substances (PFAS) in the gas and liquid phase by iodide-adduct chemical ionization mass spectrometry (CIMS)" QA Tracking # D-EMMD-0031657-QP-1-0 as well as "Operation of the Aerodyne/Tofwerk Chemical Ionization Mass Spectrometer" (QA Tracking #D-EMMD-AQB-013-SOP-02). Whole air will be analyzed under full-scan (e.g. m/z 50-950), chemical ionization (I-) -MS conditions. Instrument parameters that are analyte-specific will be recorded in the instrument log book and LRB of PI (or approved user). Method development and methods deemed appropriate for non-targeted analysis will be recorded in the LRB of the PI. Preliminary identification of compounds will be completed by recording the m/z values of peaks of interest, compared to in house, putative identification database. No internal standard masses (i.e. 'mass added'), nor peak areas will be reported even if added to these samples.

Targeted and non-Targeted PFAS

The aqueous midget impinger sample will be analyzed for targeted and non-targeted PFAS compounds. The analytical procedures used for this project are detailed in the following ORD SOPs:

- D-EMMD-PHCB-062-SOP-01: *Method for Extraction and Analysis of Perfluoroethercarboxylic acids (PFECAs) from Surface Water, Well Water and Waste Water by Ultra-High Performance Liquid Chromatography (UPLC)-Tandem Mass Spectrometry (MS/MS)*
- D-EMMD-PHCB-043-SOP-03: *Improved Method for Extraction and Analysis of Perfluorinated Compounds (PFCs) from Surface Waters and Well Water by Ultra-High Performance Liquid Chromatography (UPLC)-Tandem Mass Spectrometry (MS/MS)*
- D-EMMD-PHCB-034-SOP-01: *Analytical method for non-targeted and suspect screening in environmental and biological samples using Time of Flight Mass Spectrometry (TOFMS)*

Targeted PFAS Analysis. In targeted analysis, PFAS analytes with known chemical structure are identified by comparison of peak area and retention times (RT) to an authentic standard obtained either from commercial sources or developed by ORD through ongoing research. ORD has developed standards for the PFAS compounds listed in Table 3. These compounds are routinely identified and quantitated during targeted PFAS analysis. This group includes PFOA and GenX which are of most interest to NYSDEC. Results are typically reported in ng/L. High concentrations that may be present in emission extractions may be reported

in µg/L and will be clearly labeled in data reports and Excel files.

Table 3. List of PFAS compounds targeted in the ORD lab.

Short Name	Chemical Name	Formula	CAS no.	Monoisotopic Mass (g/mol)
GenX	Perfluoro(2-methyl-3-oxahexanoic) acid	C ₆ HF ₁₁ O ₃	13252-13-6	329.9750
PFBA	Perfluorobutanoic Acid	C ₄ HF ₇ O ₂	375-22-4	213.9865
PFPeA	Perfluoropentanoic Acid	C ₅ HF ₉ O ₂	2706-90-3	263.9833
PFHxA	Perfluorohexanoic Acid	C ₆ HF ₁₁ O ₂	307-24-4	313.9801
PFHpA	Perfluoroheptanoic Acid	C ₇ HF ₁₃ O ₂	375-85-9	363.9769
PFOA	Perfluorooctanoic Acid	C ₈ HF ₁₅ O ₂	335-67-1	413.9737
PFNA	Perfluorononanoic Acid	C ₉ HF ₁₇ O ₂	375-95-1	463.9705
PFDA	Perfluorodecanoic Acid	C ₁₀ HF ₁₉ O ₂	335-76-2	513.9673
PFBS	Perfluorobutane Sulfonate	C ₄ HF ₉ SO ₃	375-73-5	299.9503
PFHxS	Perfluorohexane Sulfonate	C ₆ HF ₁₃ SO ₃	355-46-4	398.9366
PFOS	Perfluorooctane Sulfonate	C ₈ HF ₁₇ SO ₃	1763-23-1	499.9375
PFUnDA	Perfluoroundecanoic acid	C ₁₁ HF ₂₁ O ₂	2058-94-8	563.9641
PRDoDA	Perfluorododecanoic	C ₁₂ HF ₂₃ O ₂	307-55-1	613.9609
PFTTrDA	Perfluorotridecanoic acid	C ₁₃ HF ₂₅ O ₂	72629-94-8	663.9577

Non-Targeted PFAS Analysis. In non-targeted analysis, detected masses have features such as the m/z values of peaks, RT, and isotope patterns, but there are no standards available to identify them. The analyst will attempt to identify them by comparing them to mass spectral libraries and/or in house, putative identifications. If a tentatively identified compound cannot be identified, its chromatographic retention times and ‘area under the curve’ are reported and the compound is listed as an unknown. Amount present is reported as relative abundance. The presence of PFAS compounds identified in non-targeted analysis are reported as abundance with no specific units. No internal standard masses (i.e. ‘mass added’), nor peak areas will be reported, even if added to these samples.

B5 Quality Control

Quality control criteria are discussed in further detail in the SOPs referenced in this document. Please refer to these specific procedures for additional details about QC for each procedure.

To ensure that supplies and consumable materials remain free of potential contaminants, process blanks including solvent blanks, matrix blanks, and trip or field blanks, as appropriate, will be analyzed with every analytical batch run in this evaluation. Results from these analyses must show that all analytes are nonconsequential. If any of these analyses yield target analyte concentrations that are of concern, the results of the entire batch will be flagged and a systematic evaluation of the materials used in the entire process will be conducted until the source of the contamination is found. Once the contaminated material has been identified, it will be replaced with a new batch or lot that has been tested to be free from contamination and the entire batch will be rerun.

B6 Instrument/Equipment Testing, Inspection, and Maintenance

The RTP MS analytical systems are tuned by the manufacturer annually during regularly scheduled preventive maintenance service, or more frequently if conditions warrant, as outlined in the appropriate SOPs. Systems are manually tuned by the operator to ensure ion intensities, relative ion abundances, mass resolution, and ion peak shape are within manufacturer’s specifications. Data on tune performance

parameters is available in the instrument log files.

B7 Instrument/Equipment Calibration and Frequency

Calibrations

Supporting equipment such as balances, weights, pipettes, thermometers for temperature monitoring, autoclaves, centrifuges, incubators, and thermocyclers require annual calibration in accordance with ORD PPM 13.4. The AEMD Metrology Laboratory provides inhouse calibrations/verifications of balances, pipettes, weights, thermocouples and flow measurement devices. It is the responsibility of the equipment users to ensure that the support equipment used has been calibrated and is within the calibration certification period.

Traceability of Standards

Standards are purchased as traceable to NIST standards, where available. Certificates of analysis received with each calibration material or reagent are maintained in logbooks stored in the laboratory where the calibration is used or stored. Calibration materials are verified using an independent or second source standard, as described in the individual analytical SOPs. It is recognized that due to the limited number of certified reference and calibration material suppliers for PFAS chemicals, a second source standard may not be available for all compounds. Research conducted under this program shall make every effort to identify and procure second source materials for calibration verification. Where a second source vendor cannot be identified, alternative approaches, for example a separate lot of the material from one vendor.

B8 Inspection/Acceptance of Supplies and Consumables

All supplies and consumable materials, such as solvents, reagents, labware, extraction cartridges, and other materials used in these analyses will be incorporated in to laboratory blank samples to assess contamination. Only materials that have been found to be reliably free from PFAS contamination will be used. For the whole air samples, materials will be used that are as free from contamination to the extent feasible; however, the novelty of the analytical approach, may result in residual analyte. This will be monitored through the preparation and analysis of process blanks as described in Section B5.

B9 Non-Direct Measurements

No secondary/existing data will be used for this project. As such this section is Not Applicable.

B10 Data Management and Reporting

AEMD will follow the procedures outlined in the NRMRL pQAPP for PFAS research. The data files are the electronic versions of these data. The electronic version of data is calculated by the instrument software and then exported to Excel. The file path(s) for where electronic data is stored will be documented in LRBs. Raw data (including electronic data on individual PC hard drives and group shared drives) will be backed up to a network or external hard drive. All data generated will be maintained by the PI, Jeff Ryan, until completion of the project. Upon completion, data will be stored in accordance with EPA's record management policy. All instrument data will be backed up to network drives routinely and will be archived along with other supporting data and relative correspondence at the completion of the study. Printed data will be referenced in LRBs, signed and dated in accordance with the Office of Research & Development's Policy and Procedure Manual Section 13.02 on Paper Laboratory Records. The LRB will be the record for any procedure conducted in the laboratory and will provide the objective, procedure details, data references and discussion for project development. Data will be recorded from these experiments as observed. Any standard, solution, or sample made during these investigations will be marked with a reference number and/or will be traceable to a specific entry in the LRB. The LRBs are the property of the EPA and will be stored in accordance with EPA's record management policy.

ORD will plan to provide data results to NYSDEC batched by analysis type as soon as they have been quality assured and cleared at EPA. Non-targeted analysis requires considerably greater processing time. The

timing and content of reports can be negotiated with NYSDEC as the project proceeds.

ORD will provide laboratory results to NYSDEC and Region 2 via a formal data report that includes a transmittal letter from the Lab Director and attached data report. The results and report will undergo a rigorous review process including internal scientific and QA review. The data report will address the following topics:

- Summary of test approach including actual test schedule and matrix, sampling and analytical methodologies and supporting information;
- Qualitative measurement results and narrative for;
 - Targeted PFAS compounds (PFOA and HFPO-DA) presence/absence, relative abundance
 - Non-targeted PFAS compounds and their relative abundance;
 - Targeted VOCs
 - Targeted and non-targeted thermal degradation products (TFE, HFP, E1)
- A summary of Quality Control testing results and analyst description of the level of confidence in the reported results.

The summary report or memorandum will be provided when all analyses and tasks described in this QAPP are completed. While a summary report is targeted within 3 months of testing, analyst test schedules and required reviews are factors that must also be considered. As a result, EPA/ORD will provide informal updates to NYSDEC and regional partners. Any discussion of findings in this context are considered preliminary and deliberative and not to be shared or released.

NYSDEC and ORD will determine the content of the final report. The data report will undergo an elevated clearance process within EPA including review by Region 2 and program offices prior to final release.

EPA/ORD communication of data report findings is limited to Region 2 and NYSDEC. ORD will consult with NYSDEC about any use of the data including internal sharing of findings.

EPA's Region 2 point of contact (POC) will coordinate communications between NYSDEC and ORD and convene meetings on an as-needed basis.

ORD's goal is to provide NYSDEC with data that is timely, of high-quality, and relevant to their regulatory actions. NYSDEC assumes responsibility for communications of findings to the public, impacted communities, water utilities, or industry.

A desk statement summarizing report findings will be prepared by EPA/ORD with review/input from the relevant Region and Program Offices prior to transmitting any data or reports. These desk statements are used by EPA communications should they receive any requests for information.

The data generated in this project may also be used by ORD for scientific presentations and publications. Before any data are made public by ORD, ORD will provide advance notification and consult with NYSDEC and Region 2 POC.

Section C. Assessment and Oversight

C1 Assessments and Response Actions

AEMD will follow the requirements described in the NRMRL pQAPP regarding project assessments. For Category A projects, a minimum of one technical systems audit (TSA) and one audit of data quality (ADQ) will be performed and coordinated by the AEMD QA Manager.

ADQs will be a random check of electronic and hand-entered data conducted by the AEMD QA Manager or

appropriate designees. These audits will focus on review of data transcription, calculation, and reporting. The AEMD QAM will report to the researcher any findings requiring corrective action. Any findings and corrective measures will be noted in the file and discussed in the final report.

Internal quality control measures described in this QAPP, implemented by the technical staff and monitored by the EPA PIs, will give information on data quality on a day-to-day basis. A secondary reviewer will be designated to QA audit the data quality prior to the AEMD QAM data audit. The responsibility for interpreting the results of these checks and resolving any potential problems is shared between the technical staff and EPA PIs. In addition, the NYSDEC field and technical staff will report any problems that could potentially affect the data quality to the EPA PIs. The EPA staff will also be responsible for identifying problems that could affect data quality or the ability to use the data upon receipt of the samples and during the analyses. Any problems that are identified will be addressed by taking actions to control the problem, identify a solution to the problem, and ameliorate losses and correct data, where possible. All of the actions taken by the EPA PIs to correct issues will be documented in LRBs as part of the project records.

TSAs or surveillance audit(s) will be conducted by the AEMD QAM or designees to assess implementation of this QAPP. Any findings will be reported to the respective EPA PIs and corrective actions will be implemented to address those findings. Ideally, the quality control measures regulating the operation of each work area will be sufficient to maintain acceptable performance and data quality. However, if a study component is not operating within the limits of acceptability, as determined by a QA assessment, a formal account of the matter must be documented by the PI as part of the project records.

The report should contain the following information:

- Description and duration of problem
- Probable cause and resolution of problem
- Statement describing data affected by problem
- Feasibility of repeating work activity and/or generating new data.

No further work may be performed until the problem has been satisfactorily resolved, and the PIs, after consult with the QA Manager as needed, has acknowledged approval to continue work.

C2 Reports to Management

The AEMD Division Director will be responsible for transmitting data results to US EPA's Region 2 once all reviews are complete.

Results of any QA audits will be reported as part of the final report. This section will summarize any errors, deficiencies, or deviations from the QA documentation that may, or may not, have an impact on the data.

Section D: Data Validation and Usability

The data will undergo QA review by a secondary reviewer that would check for completeness, calculations, and transcription errors before delivering the data to US EPA Region 2. The data will be reported with appropriate data quality flags, as needed.

D1 Data Review, Verification, and Validation

Field Sample Data Review

Sampling data will be reviewed both in the field and upon return to RTP. In the field, there will be two ORD samplers – Jeff Ryan and Ken Krebs. Each will review the other's standardized sampling data collection sheets for accuracy and completeness. CoCs will also be reviewed in the field as well as

when received in RTP. CoCs will be reviewed for any discrepancies as described in Section B3. Noted discrepancies will be documented either on the chain of custody or in the research notebook.

Data Reduction

Sampling data reduction (final sample volumes, calculated concentrations, summary tables, etc) will also be independently reviewed. Jeff Ryan will be responsible for the majority of the data reduction. Independent data reviewers of his work include Ken Krebs, John Offenberg, Ingrid George and Libby Nessley.

Data Verification

The goal of data verification is to ensure that complete and accurate analytical information is available for all samples analyzed by the laboratory. Data verification begins during and after the period of analysis, and data entry into the Excel spreadsheet. The key personnel of the analytical team will perform the first level of review, ensuring that all data have been verified. The mechanisms used for all data transcriptions and transmissions will be reviewed, and a random subset of all transcriptions checked.

Once the chemical measurement data have been exported into a spreadsheet (e.g. Excel), the following QA/QC checks to verify the data will be carried out:

- Sample ID checks to verify that all Sample IDs with reported data are valid Sample IDs, i.e., they were logged in as received from NYSDEC (Ingrid George, Mark Strynar),
- Missing data checks to verify that all Sample IDs received from the field either had a full set of analytical data reported or were disqualified, as documented in the CoC data or in LRBs (Jeff Ryan),
- Duplicate data checks, to verify that the same analytical data were not imported into the Excel spreadsheet twice for a given sample (Jeff Ryan, Dennis Tabor),
- Out-of-range checks, to verify that all data for data fields limited to a code set did not violate that code set (Jeff Ryan, Ken Krebs, Dennis Tabor).

Data quality flags will be assigned to each chemical measurement record as needed to identify the quality and usability of the record. Data quality flags will be assigned as defined in each report, if necessary.

D2 Verification and Validation Methods

Data Validation

In order to non-quantitatively identify an analyte, a minimum signal to noise (S/N) ratio for any ratio (e.g., sample to blank, sample to instrumental noise) will be initially defined as 10:1 and may be adjusted as appropriate by the analyst. The minimum S/N ratio ultimately applied will be recorded in a research notebook.

The validation of the data will be encompassed in the results of the QC samples in each shipment of sample unknowns since these QC samples will reflect all the sample preparation, shipping, storage, and handling of actual field samples. For laboratory and field blanks, if the background level for a given target analyte is unacceptably high (i.e., S/N is greater than 10:1), the target analyte results for all samples affected by this background will be flagged. The recoveries of analytes in these field samples will be a reflection of recovery of analytes throughout the entire process. In addition, the recovery of the internal standard (IS) compounds will demonstrate the method performance on a sample by sample basis. Since the ISs are the labeled version of a representative analyte of each class, the IS recoveries may be used to effectively assess losses during analytical procedures on a sample by sample basis.

Verification and Validation Methods

In the laboratory, the data will be verified and checked at several levels. The instrument operator will complete a first pass assessment of accuracy of identification of analytes in samples. This will be done on-screen using an automated procedure, when possible, where the system pages through the data for identification of each analyte in each sample. If adjustments are needed, this will be done manually by the analyst. Electronic output will include a copy of the method, a copy of each calibration curve with equation and fit printed, run list, and a summary of the quantitation for each analyte. As noted above, the electronic files will be stored on the instrument computer and backed up routinely.

The technical reviewer will review data for accuracy in identification and quantification. This reviewer will monitor retention time, mass transition, and qualifier ion ratios.

The LC-MS/MS analytical data for samples are preprocessed, and initially reviewed using spreadsheet software; this is a three-step process which can be described as follows:

- The LC-MS/MS summary data are electronically transferred into an Excel spreadsheet or exported as a delimited text file that can be read in Excel. This consists of the analysis date, the sample identification number and classification (e.g., blank, QC, calibration, unknown), target analyte names, analyte and internal standard (IS) peak area counts, analyte/IS peak area ratios, quantitation ion/qualifier ion ratio, and concentration of analyte in ng/L. The first reviewer assures that this electronic transfer has been made accurately and completely.
- The first reviewer hand-enters into the spreadsheet any ancillary analytical data required. Any hand-entered data will be checked by a second analyst. The spreadsheet functions as a user-friendly interface for data entry and also imposes uniformity on the reported data. For the samples, the spreadsheet requests data values in specific units that have a uniform accuracy, i.e., number of significant digits. The straight-forward design of the spreadsheet also permits all the data from any given analytical run to be reviewed by the task leaders without requiring them to invest time learning new software.
- The final, tentative analyte identifications are reported as a tentatively identified compound (name), or empirical formula, along with corresponding retention time (where appropriate) and volume/mass/pressure of sample used in the analysis.

Validation of the data will be conducted by evaluating the S/N ratios and ensuring they fall within the acceptance criteria mentioned above (i.e., at least 10:1). Results that fall outside acceptance criteria will be flagged.

Percent recoveries will be calculated by the following:

$$(\text{Recovered Mass}/\text{Spiked Mass}) \times 100 = \text{Percent recovery}$$

D3 Reconciliation with User Requirements

The AEMD PI will review the reported data to verify that QC checks have been documented and that acceptance criteria have been met and that data has been qualified appropriately using qualifiers.

The technical lead shall use the results of the data review, verification, and validation process to assess whether the data quality meets the project requirements and thereby the user requirements. If there are data quality issues that may impact their use, the impact will be evaluated by the technical lead. The technical lead may seek assistance from QA staff as needed.